PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. _____

Project No. A-3558 GTRI/~~GTX~~ DATE 06 / 16 / 83

Project Director: W. S. Lewis ~~School~~/Lab EMSL

Sponsor: U. S. Department of Interior; National Park Service

Type Agreement: P. O. PX-0001-3-0571 under Contract No. CX-0001-2-0036

Award Period: From 5/23/83 To ~~8/23/83~~ 2/23/84 (Performance) ~~11/23/83~~ 2/23/84 (Reports)

Sponsor Amount:	This Change	Total to Date
Estimated: $	15,000	$ 15,000
Funded: $	15,000	$ 15,000

Cost Sharing Amount: $ N/A Cost Sharing No: _____

Title: Materials Degradation Field Kit for Parks with Emphasis on Laboratory Confirmation of Nitrogen Compounds.

ADMINISTRATIVE DATA OCA Contact Frank Huff X4820

1) Sponsor Technical Contact:

Susan I. Sherwood
Park Historic Architecture (422)
National Park Service
Department of Interior
Washington, D.C. 20240
(202) 343-8149

2) Sponsor Admin/Contractual Matters:

Judy Bryan
Administrative Services Div. (230)
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Washington, D.C. 20240
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Defense Priority Rating: N/A Military Security Classification: N/A

(or) Company/Industrial Proprietary: _____

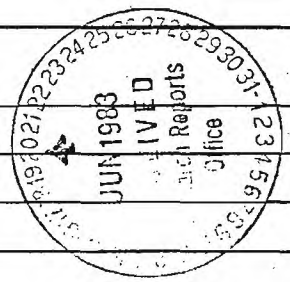
RESTRICTIONS

See Attached Government Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with Sponsor if acquisition cost is $1,000 or more; however none is proposed.

COMMENTS:



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FORM OCA 4:383

)RGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 3/28/84

ct No. A-3558 School/Lab EMSL

ides Subproject No.(s)

ct Director(s) Dr. W. S. Lewis GTRI / ~~GXX~~

nsor U.S. Department of Interior, National Park Service

"Materials Degradation Field Kit for Parks with Emphasis on Laboratory Confirmation of Nitrogen Compounds"

ctive Completion Date: 8/23/83 (Performance) 2/23/84* (Reports)

nt/Contract Closeout Actions Remaining:

*Project reporting period was verbally extended thru 2/29/84

- [ ] None
- [X] Final Invoice or Final Fiscal Report
- [X] Closing Documents
- [X] Final Report of Inventions
- [X] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other

ntinues Project No. Continued by Project No.

PIES TO:

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rm OCA 60:1028

A-3558

Georgia Institute of Technology
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

July 5, 1983

Ms. Susan Sherwood
Park Historic Architecture (422)
National Park Service
Department of the Interior
Washington, D.C. 20240

Re: Contract No. CX-001-2-0036
Materials Degradation Field
Kit for Parks with Emphasis
on Laboratory Confirmation
of Nitrogen Compounds.

Dear Ms. Sherwood:

We are reporting our progress under this contract for June, 1983.

Program initiation began on 6 June 1983, our first priority was to assemble a data base of materials effects of acid rain. This has been accomplished resulting in about 300 citations, over 100 of these were of sufficient relevance to warrant evaluation. This evaluation is about 80% complete. We have found that some European Conference proceedings are difficult to locate.

We initiated an investigation of analytical methods suitable for determination of nitrogen compounds on stone, emphasis is on sensitivity, interferences and ease of use by non technical personnel. We are seeking established methodology which may be adapted for our use. A number of potential methods have been assembled and are being evaluated.

We attended relevant sessions of the APCA conference held in Atlanta, June 21-24. We met with Yocom, Baer, Stankunas Haynie, and others who are pursuing similar research. This was quite productive and we agreed to present the results of this research at the APCA conference next year in San Francisco, subject to continued funding and approval. Our proposal "Field Measurement of Materials Degradation" has

been approved for presentation at the APT conference in Nashville, TN on 29 September 1983 at 9:45 a.m.

We have allocated to appropriate personnel the tasks of evaluating the mitigation of acidic effects by NH_4^+, electron microprobe determination of nitrogen on stone surfaces and tools one would require for sampling and evaluating stone surfaces in situ.

Budget Summary

		Percent
Total	$15,000	100
Expended, June	3,539	24
Remaining	11,461	76

Respectfully submitted,

W.S. Lewis, Project Director

Approved:

T. L. Starr, Chief
Materials Science Division
Energy and Materials Sciences
Laboratory

A-3558

ENGINEERING EXPERIMENT STATION
Georgia Institute of Technology
A Unit of the University System of Georgia
Atlanta, Georgia 30332

September 6, 1983

Ms. Susan Sherwood
Park Historic Architecture (422)
National Park Service
Department of the Interior
Washington, D.C. 20240

Re: Contract No. CX-001-2-0036
Materials Degradation Field Kit for Parks with Emphasis on Laboratory Confirmation of Nitrogen Compounds

Dear Ms. Sherwood:

We are reporting our progress under this contract for August 1983.

We have completed our design considerations for a field kit and are assembling costs for various options. We have also completed an outline for the final report and have begun assembling a draft report for your consideration. The resignation of Dr. T.L. Wu has created a gap in our personnel but we will be able to meet the original project deadlines. We will present our paper on the field kit in Nashville. Tom and I both plan to attend.

Budget Summary

		Percent
Total	$15,000	100
Expended to Date	$12,029	80
Remaining	$ 2,970	20

Respectfully submitted.

W. S. Lewis, Project Director

Approved:

T.L. Starr, Chief
Materials Science Division
Energy and Materials Sciences Laboratory

FINAL REPORT (PART I)
PROJECT NO. A-3558

DETERMINATION OF NITROGEN COMPOUNDS ON STONE AND METAL

By

W. S. Lewis
T. L. Starr

Under

NPS Contract No. CX-0001-2-0036
Work Assignment #1

FEBRUARY 1984

GEORGIA INSTITUTE OF TECHNOLOGY
A Unit of the University System of Georgia
Engineering Experiment Station
Atlanta, Georgia 30332

DETERMINATION OF NITROGEN COMPOUNDS ON STONE AND METAL

by

W.S. Lewis and T.L. Starr
Energy and Materials Sciences Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

FINAL REPORT (PART I)

NPS Contract No. CX-0001-2-0036
Work Assignment #1

Georgia Tech Project No. A-3558

February 1984

I. INTRODUCTION

Instrumental analytical techniques such as X-ray fluorescence are commonly used to perform elemental analysis of stone and metal sample coupons. While providing rapid and accurate measurement for sulfur and other elements heavier than fluorine, this technique does not detect nitrogen compounds, which are known to be important components of acid precipitation.

Without methods to measure nitrogen compounds on the surfaces of exposed stone and metal materials, research results may tend to be biased against the role of atmospheric nitrogen in materials deterioration.

We have identified analytical methods which are suitable for the determination of nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) ions on stone and metal samples. The methods examined are for both laboratory and in situ measurements. We have summarized sensitivity, selectivity, restrictions on sample size, status of sample after analysis, unit cost per analysis, time and level of skill for implementation of each technique.

Ashton (1) has recently reviewed the important microenvironmental parameters related to the durability of building materials. These parameters are identified as temperature, moisture, solar radiation and pollution deposition on the material surface. The role of nitrogen compounds in deterioration of building materials is not well defined.

II. DETERMINATION OF NITROGEN COMPOUNDS

Laboratory determination of nitrogen compounds on stone and metal surfaces will require taking small samples, either corings (stone) or surface scrapings (stone/metal). Typically the quantity of sample required is defined by the technique used for quantification and the amount of information one seeks to obtain. Generally samples of a few tenths of a gram of the feature of interest will be sufficient. In some instances it may be desirable to make color photographs of the resource indicating where the samples were taken. These photographs along with the samples may be archived for later analysis.

We limit our discussion to nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+) and total nitrogen without regard to the source of these ions. Discussions of the role of acid deposition (2-12) and salt migration of nitrogen compounds (13-17) may be found in the references indicated.

Detection limits as discussed here refer to micrograms (μg) of sample in a milliliter (ml) of sample solution (ppm). We would anticipate that a minimum sample size would be 1 g dissolved in 100 ml of a suitable solution, hence the dilution factor would be 100:1. In some cases this dilution factor would be less.

Laboratory Methods

A variety of instrumental methods are available for

the analysis of stone and metal samples. Adler (18) has recently reviewed the fundamentals of the more common techniques.

X-ray diffraction analysis (XRDA) consists of measuring the intensity and angular distribution of monochromatic x-rays diffracted by a crystalline material. This distribution results in a "fingerprint" of the material being analyzed. Positive identification of the crystal composition is made by comparing the diffraction pattern to those listed in a data file such as that published by JCPDS (19). The major advantage of this technique is that the chemical composition of the material is determined-not just the atoms present but the specific compound present - (e.g. nitrate and ammonium salts are readily distinguishable). A significant disadvantage is that only crystalline nitrogen compounds are detected, not nitrogen associated with amorphous materials.

This method is adaptable to quantitative analysis with some limitations. The diffracted x-ray intensities are proportional to the amount of a compound present in a sample but correction for absorption and scattering of mixtures is difficult. This method is best used with a directly quantitative elemental analysis method for total nitrogen present such as the electron microprobe (EM).

Total nitrogen content may be determined using a wavelength dispersive x-ray analyzer such as found

associated with an electron microprobe (EM). Analysis by EM consists of bombarding the surface of a small sample with high energy electrons, dispersing the resulting x-rays by wavelength and measuring the intensity of these x-rays as a function of wavelength. While similar in many respects to the popular combination of scanning electron microscopy with x-ray analysis (SEM/XRA), the wavelength dispersive analyzer in EM allows detection of lighter elements, such as nitrogen, which cannot be detected by SEM/XRA. The electron beam incident on the sample is highly collimated. Typical beam diameters are variable from 1 to 300 microns (μm). The beam penetration into the surface of the specimen is usually 1 to 2 μm, hence this is a true surface technique. Sensitivity of the method is dependent upon the volume analyzed. Typically 10 picograms (10^{-14}g) may be detected in a 1 μm area. We find precision for nitrogen to be better than 0.1% of the volume analyzed.

Samples for EM analysis may be up to one inch in diameter and need to be reasonably flat. A thin film of graphite (1 μm) is vacuum deposited on the surface to make the sample electrically conductive. Samples may be single grains of stone or metal salts which may be extracted from the surface by scraping or by using an adhesive material such as replicating tape.

The use of electron microprobe for crustal analysis of stone has been reported for limestone (20) and marble (21)

but nitrogen was not determined.

Ion Chromatography (IC) employs the motion of solvent (mobile phase) carrying a sample solution through an ion selective column (stationary phase). The solvent and column are optimized for a particular sample depending upon whether cations or anions are to be determined. For a particular set of conditions, different ions have different times of passage through the column. This time is called the retention time. The ions are quantified by measuring the change in electrical conductivity of the solvent as the ions elute from the column. IC is commercially available and detection limits are typically less than 0.1 ppm for NO_3^- and NH_4^+. There are no known interferences for this method as separation of different ions is by charge and size. Methods have been published for the analysis of both NO_3^- (22, 23) and NH_4^+ (24) which are applicable to stone and metal samples. An advantage is that a number of ions may be determined from a single aliquot. Some of these are: Cl^-, NO_3^-, NO_2 , SO_4^{-2}, CO_3^{-2}, HCO_3^-, HSO_4^- as anions and NH_4^+, Na^+, K^+, Mg^{+2}, Ca^{+2}, as cations. The detection limits are similar.

Ion specific electrodes (ISE) are available for determining both NO_3^- and NH_4^+ in solutions. The detection limit for NO_3^- is about 0.1 ppm but due to numerous interferences (Cl^-, CO_3^{-2}, HCO_3^- and HS^-) chemical pretreatment

of the sample solution is required and actual sensitivity is dependent upon the relative concentrations of other ions (25). Guidobaldi (26) noted that several ions interfere with this analysis and that the response is pH dependant. Hence he does not recommend this technique for stone samples. De Vecci (17) was able to determine NO_3^- on marble effluorescences at a level of several hundred ppm in the presence of 0.03 to 6.04% Cl^-. Determination of NO_3^- by ISE in Wisconsin Limestone has also been reported (27).

Detection limits for NH_4^+ by ISE are typically about 0.02 ppm. There are no reported interferences (25) except for volatile amines which are not likely to be found on stone and metal surfaces. We have not seen the application of this method to stone and metal samples but it has been widely used for soils and clays (28, 29).

Due to numerous interferences for NO_3^- ISE and pH dependent response for both NO_3^- and NH_4^+ ISE, we would not anticipate their adaption to in-situ analysis. However, their relatively low cost and ease of use would make ISE's attractive for multiple sample analysis.

Diffuse reflectance spectrometry utilizes the radiation reflected from a surface being illuminated by the sun or an artificial light source in some solid angle. This reflected radiation contains information about the chemical nature of the reflecting surface. (The reflection is said

to be diffuse when the angle of reflection is not equal the angle of incidence, as is the case for roughened, unpolished surfaces). Near infrared reflectance (NIR) is widely used for in situ mineralogical analysis (30-34). NIR spectra contain information about the vibrational environment of hydroxyl groups (-OH). The mid infrared spectral region (2.5 - 20 μm) contains substantially more information about the chemical composition of the surface. Nitrate and ammonium salts have strong absorption bands in this region, as do sulfates. Table 1 indicates general absorption regions for important inorganic anions.

Figure 1 is preliminary results of reflectance spectra of nitrate and sulfate deposited on steel surfaces. These laboratory spectra, taken with a diffuse reflectance accessory, illustrate the specific information about surface composition available.

We are investigating this technique for the detection of contaminants on steel, as part of a concurrent Federal Highway Administration program (35).

We have reviewed the various colorimetric methods for determining nitrogen compounds and have selected those which show promise for stone and metal samples. High sensitivity and freedom from anticipated intereferences are primary requirements. Samples for chemical analysis would consist of corings or or scrapings from areas of the resource which are indicative of phenomena of interest. Sample size

would typically be a few grams for quantification. Analysis by the methods discussed here requires relatively inexpensive equipment. They might prove labor intensive if a large number of samples are analyzed, however reagents can be prepared and relatively unskilled personnel can be trained in their use.

Guidobaldi (26) has used a colorimetric method for NO_3^- using chromotropic acid and reports a detection limit of about 2 ppm using an analytical wavelength of 0.41-0.42 μm. Considerably lower detection limits (0.1 ppm) may be obtained using 0.357 μm (36). This method determines both NO_3^- and NO_2^- and we suggest adaption for field use. The Hach method (37) is based on cadmium reduction of nitrate to nitrite with quantitation at 0.54 μm. The method reported is of lower sensitivity (detection limit of 20 ppm) but kits are commercially available (38). Kits are also available from Hach with a detection limit of 10 ppm.

For NH_4^+ determination, the traditional Nessler reagent is to be avoided due to possible interferences from Pb^{+2}, Mg^{+2}, Fe^{-2} and S^{-2} which may be present in stone and metal samples. Weatherburn (39) has reported the use of sodium hypochlorite and phenol which forms indophenol blue in the presence of traces of ammonia. The method uses sodium nitroprusside as a catalyst and has a reported detection limit of 0.001 ppm at 0.625 μm.

Table 2 is a summary of methods discussed. The detection limits are the best reported values. The estimated cost per sample is presented in Table 3 along with information derived. The unit analysis cost considers both equipment cost and level of skill required for analysis.

III. SUMMARY AND CONCLUSIONS

Our review of analytical methods for determining nitrogen compounds indicates that several techniques are adaptable for use with stone and metal samples. Method selection for nitrogen quantification would be dependent upon sampling restrictions imposed by the nature of the resource. Colorimetric techniques requiring a few milligrams of sample may be adapted for field use. For laboratory use, ion chromatography provides sensitive and selective analysis with a reasonably low per-sample cost.

The methods presented allow for both in situ analysis with appropriate equipment or sampling from the resource and submission to a laboratory for analysis. We anticipate that the most time consuming process would be selection of actual sampling sites associated with a specific resource. This selection must be done in such a manner as to assure that the samples selected are characteristic of the deterioration phenomena of interest.

Fully trained personnel should be able to obtain a sample in a few minutes. Sample analysis by fully trained personnel would require a few hours at most. Park personnel with good mechanical skills should be trainable in sampling methodology in a few hours. Training personnel in field characterization techniques e.g., ISE and colorimetry, would require approximately 40 hours of instruction for

routine analysis provided personnel had some background in science at the level of high school chemistry and physics.

Table 1.

Infrared Absorption of Selected Ions

Anion	Absorption Peak Region (micrometers, μM)
CO_3^{-2}, Carbonate	6.8 - 7.2; 11.3 - 11.7
SO_4^{-2}, Sulfate	8.5 - 10.0; 14.7 - 16.5
NO_3^-, Nitrate	6.0 - 8.0; 11.5 - 13.0
NO_2^-, Nitrite	8.0 - 8.2; 11.9 - 12.5
NH_4^+, Ammonium	3.0 - 3.3; 6.8 - 7.5

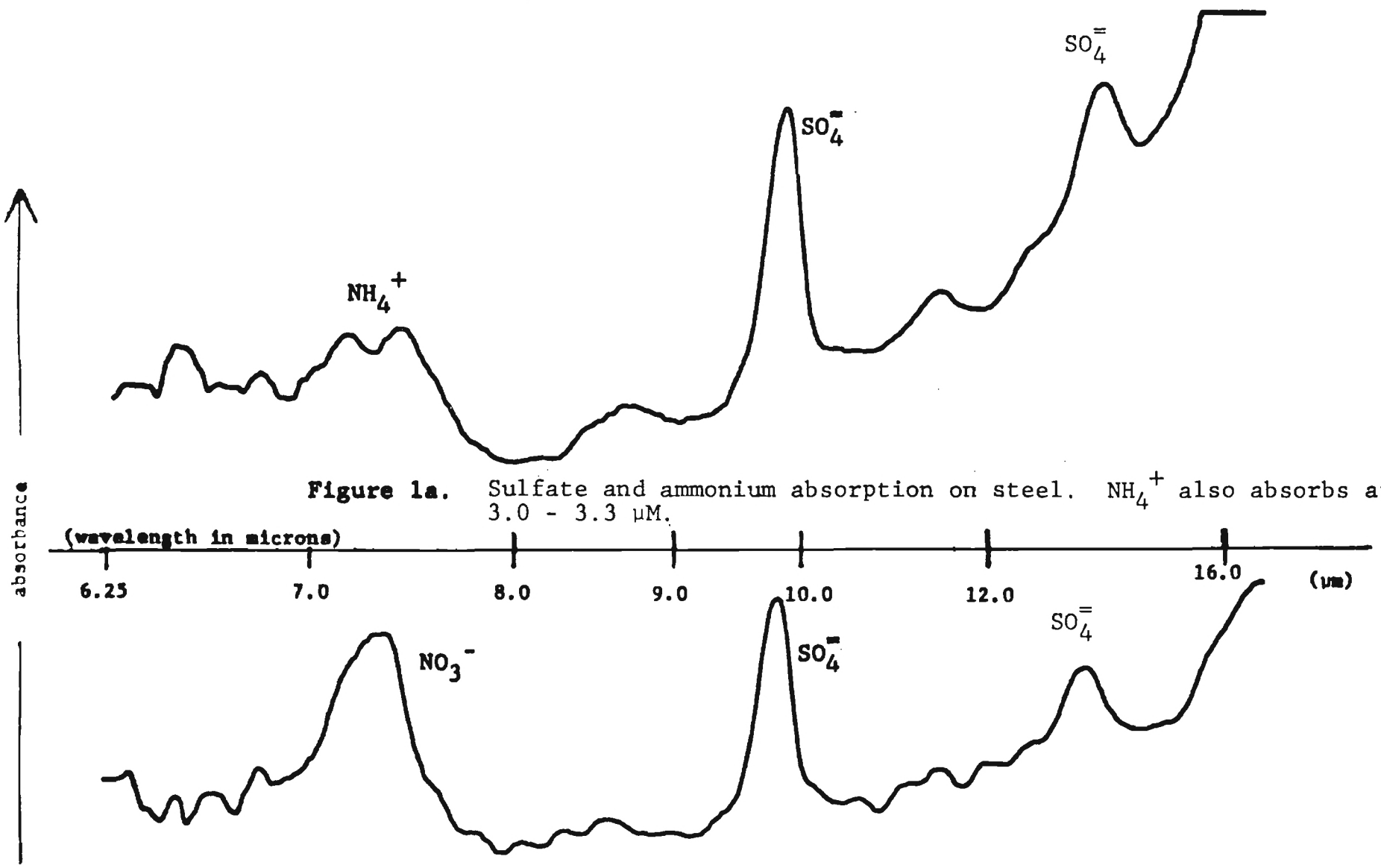

Figure 1a. Sulfate and ammonium absorption on steel. NH_4^+ also absorbs at 3.0 - 3.3 μM.

Figure 1b. Sulfate and nitrate absorption on steel.

Nitrogen Compound	Detection limits[a] (ppm)	Method	Equipment Required	Minimum[c] Sample	Portable	Sample Preparation
Total Nitrogen	[b] (10^{-14}g)	EM	Electron probe microanalyzer with wavelength dispersive x-ray analyzer, ancillary equipment.	very small	NO	SOME
NO_3^-, NO^-_2 NH_4^+	10,000 (1%)	XRDA	x-ray diffraction analyzer with ancillary equipment	1g	NO	NO
NO_3^-, NO_2^- NH_4^+	10	IC	Ion chromatograph with ancillary equipment	1g	NO	YES
NO_3^- and NO_2^-	1	ISE	Nitrate Ion Specific Electrode, mV meter, reagents, accessories.	1g	YES	YES
NH_4^+	<2	ISE	Ammonia Ion Specific Electrode, meter reagents, accessories. Used with meter above.	1g	YES	YES
NO_3^-	<20 (.357μm) <500 (.415μm)	Colorimeter	Colorimeter, reagents, accessories wavelengths less than 0.4μM available on laboratory instruments.	1g	YES	YES
NH_4^+	<.1 (.625μm)	Colorimeter	Colorimeter, reagents, accessories	1g	YES	YES
NO_3^- (NH_4^+)	[d] ($ng\text{-}cm^{-2}$)	IR	IR spectrometer with diffuse reflectance accessory or radiometer and ancillary equipment for field measurement.	small	(YES)	(NO)

a = micrograms per gram sample
b = discussed in text
c = estimate based on 10:1 dilution
d = approximate, method is under development

Table 2. Methods Summary

Method	Information Obtained	Equipment Cost	1 Sample	Multiple Samples	[b]Implementation Time
EM	Total elemental composition, morphology	$150,000	$100	$100	now
XRDA	Relative composition of all crystalline material	$150,000	$ 75	$ 75	now
IC	Concentration of all ions in solution	$ 60,000	$100	$ 25	3 months
ISE	NO_3^- + NO_2^-, NH_4^+ only	$ 3,000	$ 50	$ 25	1 month
Colorimetry	NO_3^- + NO_2^-, NH_4^+ only	$ 3,000	$ 50	$ 25	1 month
[a]IR	Relative concentrations of absorbing specie.	$ 12,000	--	--	---

[a]method under development

[b]time required for method implementation for stone and metal samples.

Table 3.

COST/ANALYSIS

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FINAL REPORT (PART II)
PROJECT NO. A-3558

MATERIALS DEGRADATION FIELD KIT FOR PARKS

By

W. S. Lewis
T. L. Starr

Under

NPS Contract No. CX-0001-2-0036
Work Assignment #1

FEBRUARY 1984

GEORGIA INSTITUTE OF TECHNOLOGY
A Unit of the University System of Georgia
Engineering Experiment Station
Atlanta, Georgia 30332

GTEES

1984

MATERIALS DEGRADATION FIELD KIT FOR PARKS

by

W.S. Lewis and T.L. Starr
Energy and Materials Sciences Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

FINAL REPORT (PART II)

NPS Contract No. CX-0001-2-0036
Work Assignment #1

Georgia Tech Project No. A-3558

February 1984

Table of Contents

I. INTRODUCTION

Material deterioration occurs as a result of physical, chemical and biological processes occuring at a material boundary. The conditions occuring at a material boundary are referred to as the material microenvironment. Ashton (1) has recently reviewed the important microenvironmental parameters relating to the durability of building materials. These parameters are temperature, moisture, solar radiation, and pollution. The inter-relation of these parameters define which of the three processes dominate in overall deterioration scheme. Our recommendations for chemical and physical testing methods are presented here for materials of interest to the National Park Service.

We present our suggested methods with projected cost vs. information derived. We further have defined here techniques for identification of important chemical and physical processes which are integrable into a field kit for resource managers. When the field kit is implemented, the Park Service will gain information about the composite rate of deterioration and steps may be taken to arrest the principal causes.

The deterioration of stone and metals may be thought of as dissolution of the material fabric. The rate at which this process occurs is generally determined by temperature, cycles of wetness and the concentration of certain ions in the pores of the fabric. It is generally agreed that the

most important ions which induce further chemical changes are:

cations: H^+, NH_4^+

anions: NO_3^-, SO_4^{-2}, Cl^-, S^{-2}

We define here methods for confirming the presence of these ions.

These chemical changes lead to changes in physical properties of the material. Dissolution and recrystallization of soluble salts lead to important physical changes in stone including surface roughness, porosity, and grain adhesion.

The corrosion of metals proceeds by an electrochemical mechanism. Metals react with oxygen in the presence of moisture and the ions identified above. This oxidation leads to observable physical changes such as pitting, patina formation, and color changes.

We have identified methods for measuring the extent to which these observables change relative to some baseline value.

II. MATERIALS DEGRADATION FIELD KIT

We present our recommendations for preliminary design of a materials degradation field kit. The use of this kit will allow park personnel to make observations of important changes in important physical and chemical properties occuring at specific resources. Kit component options include reagents and apparatus for performing chemical tests, apparatus for performing physical tests and tools for taking small samples.

Design Criteria

Design criteria for the kit is based on its expected use. The field kit will be used by non-technical personnel, at multiple sites of high cultural value, and intermittently over a period of several years. The kit should provide a measure of the degradation rate of a material, sufficiently accurate to allow the resource manager to identify the need to seek expert consultation. Additionally, the field kit should provide tools for sampling the resource for archiving and laboratory analysis, and should allow monitoring of the effects and effectiveness of mitigative treatments applied to a resource. Design criteria identified include:

1) low level of technical complexity,
2) well defined procedures,
3) complete and self contained,
4) low cost per kit,
5) compact and portable,

6) stable or locally available components,

7) minimally destructive of surface,

8) measurement of critical degradation parameters,

9) rugged and quantitative techniques.

These criteria have been used as the basis for evaluation of potential field techniques. Materials of primary interest are stone (or masonry) and metal although methods included in the kit may be useful for other materials as well.

Deterioration occurs as a result of intrusion of material antagonists into the microenvironment. Various phenomena are responsible for this intrusion into the material boundary such as acid deposition, salt recrystallization, etc. This intrusion results in a change in material chemical or physical properties. The field kit allows for observations to be made of these changes. Associated with each observation are a set of measurable parameters which are determined over a period of time. These measurable parameters allow resource managers to place a numerical value on an observation using kit components. Maintaining records of values obtained for observations will allow resource managers to take appropriate action when trends are discovered that indicate progressive material damage.

We have identified parameters which can be measured and that are important in the deterioration of stone and metal.

Sampling Methods

We considered the surface sampling methods which are least damaging to material resources. The samples taken may be archived, sent to a laboratory for analysis, or analyzed at the site depending upon kit options implemented. Photographs of areas sampled should be taken to provide reference for future sampling. Applicable sampling techniques are listed in Tables 1 and 7 with an indication of their effect on the surface, the information that can be obtained, and associated costs. The sampling methods selected are adaptable to either stone or metal resources, although some variation in the sampling technique would be anticipated.

The least damaging mechanical sampling method would be accomplished using replicating tape. This is a polymer film made from cellulose acetate, polyvinyl alcohol or polystyrene which softens when treated with acetone.

To replicate a sample surface an appropriate size piece of tape is cut. This is held horizontally with the tweezers while several drops of acetone are applied to the surface. When the tape appears frosty, the acetone is dumped off and this side is pressed against the surface to be replicated. The tape is held firmly against the surface for about 1 minute with the thumb or a soft piece of material (foam), then peeled from the surface using a pick and tweezers, and allowed to air dry for 10 minutes. If any surface material

has adhered, the replication process may be repeated on the same spot until a replica containing no visible adherent material is obtained. Surface samples taken in this manner may be archived or sent to an appropriate facility for analysis.

Tapes containing adherent material provide microscopic samples for analysis by identification of characteristic X-rays, using either the electron microprobe (EM) or scanning electron microscope (SEM). The number of adherent particles per unit surface area may provide a measure of grain adhesion.

Successful replicas containing no adherent material reproduce the surface topography on the bottom of the tape. These may be examined using conventional microscopy or SEM to provide detailed morphological structure. Figure 1 is an SEM of a metal surface replica. In the field, a measure of surface roughness can be obtained from the replica using a special caliper.

Samples may be scraped from the surface and captured in a sealable plastic vial. Implementation would require sampling from a specified area by defining the area with a template or the end of the scraper. Area sampling will eliminate the need for weighing in field analysis as all results may be recorded in mass per unit area ($\mu g/cm^2$). The area sampled will depend upon the sensitivity of the analysis to be performed. Typically quantities are in the range of 0.1 to 5 grams; this amount may be estimated using guidelines

for a particular material type. Samples obtained in this manner may be archived, sent to a laboratory for quantitative analysis or analyzed either qualitatively at the site using appropriate reagents or semi-quantitatively at the site using portable instruments. These options are discussed below. The areas sampled should be documented for future reference. Scrapings obtained can provide information on the chemical composition and total quantity of soluble salts in a unit surface area. Implementation of this sampling method will require development of techniques applicable to stone, masonry and metal resources.

In some instances it may be desirable to obtain core samples of the resource. We have elected a scheme which avoids this but coring kits are available from 1/8" and larger which will fit a hand drill. Battery powered hand drills are available. Implementation of this method will require development of a mount to ensure smooth coring.

Table 2 is a list of tools required for mechanical sampling with an estimated cost per item. Using this table we estimate the cost for inclusion of materials to implement each method as:

Method	Material Cost
Replication	$ 80
Scraping	$ 30
Coring	$115

This does not include development cost incurred in defining how implementation should proceed but illustrates the sum of

appropriate materials cost.

Methods which associate a measurable parameter with an observation but are not intended to remove gross quantities of material from the surface may be discussed as non-mechanical sampling methods. These methods include chemical spot tests and those optical methods which result in an observation of chemical composition of a unit of a surface area. Applicable non-mechanical sampling methods are listed in Table 3.

We have selected chemical spot test for the ions which are generally agreed to be important in the deterioration of stone, masonry and metal. Chemical spot tests are qualitative or semi-quantitative observations of ion concentrations on the surface of a material. With the exception of pH measurements, the chemistry used in these spot tests is recommended for laboratory quantification. Table 4 is a summary of these tests. The estimated detection limits are orders of magnitude estimates based on our experience in implementing these tests on steel panels.

The test for pH (H^+) is semi-quantitative. The pH paper is pressed firmly on a moist surface and interpreted by the color code. Lead acetate paper would be used in a similar manner to confirm the presence of sulfide (S^{-2}) on a moist surface. Both of these test materials are readily available commercially. Spot tests for other ions would provide confirmation of the presence of these ions at the levels

required for a visual indication of a color change. Surface sampling would be accomplished by wetting the center of a piece of filter paper with 1 N HCl or deionized water, pressing this paper firmly against the surface to be measured to leach soluble salts from the surface. The wetted paper contains an aliquot of soluble ions in the surface area defined. This paper is then treated with specific reagents or combinations of reagents to give confirmation of the desired ion by observing the color change. The specific reagents may be added dropwise or by pressing together with reagent impregnated tickets made from an appropriate material. The time required for color development is typically 3 to 5 minutes, the intensity of the developed color is proportional to the quantity of the specific ion leached from the surface. Spot tests may be used in conjunction with color charts to provide a semi-quantitative estimate of the quantity of a specific ion present on a surface. The chemistry schemes we have selected for spot tests are those which are best suited for stone and metal samples and with suitable modification are also recommended for quantification as discussed below. We have implemented the spot tests for sulfate and chloride qualitatively as part of our concurrent Federal Highway Administration contract (2).

Implementation of spot test for semi-quantitative analysis (e.g. using color charts) will require identifying appropriate substrates for carrying out the reactions,

determining the anticipated expiration time for reagents, developing charts for color comparison for each ion of interest, and clearly defining methodology for performing this particular type of testing in an objective, reproducible manner (Table 1). Our implementation of sulfate and chloride has been on 25 mm filter paper. Nitrate, for example, could not be implemented on this substrate as the reagent vehicle is diluted sulfuric acid which attacks the paper.

The optical methods of observing chemical changes of the nature of the surface are those which involve a change in the wavelength or intensity of reflected or absorbed radiation (light).

Color is our perception of reflected radiation in the visible region. Changes in color are subjective hence we require techniques which allow for assignment of a numerical value to the color of a sample. The most important color system is the CIE system (3). It is based on the three dimensional nature of color composition, that is color may be represented by three coordinates in color space that represent the amounts of the three primary colors composing the reflected light. These three numerical values are called the tristimulus values. They are designated as:

1) X which is hue, the aspect that allows color to be identified with regions of the spectrum,
2) Y which is brightness, a measure of the lightness response or luminosity,

3) Z which is saturation, the excitation purity.

The surface color may be measured relative to a reference standard and tristimulus values calculated. Typically these values are measured from 0.38 to 0.78 μm as this is the visible region. Color standards can be developed for specific stone and metal types which would be used in visually assigning a number or a set of X, Y, Z values which are closest to the resource under observation. Spectral regions other than the visible regions may be used, however, the observation would be made using instruments as discussed below.

Diffuse reflectance spectrometry utilizes the radiation reflected from a surface being illuminated by the sun or an artificial light source in some solid angle. This reflected radiation contains information about the chemical nature of the reflecting surface. (The reflection is said to be diffuse when the angle of reflection is not equal to the angle of incidence, as is the case for roughened, unpolished surfaces). Near infrared reflectance (NIR) is widely used for in situ mineralogical analysis (4 - 8). NIR spectra contain information about the vibrational environment of hydroxyl groups (-OH). The mid infrared spectral region (2.5 - 20μm) contains substantially more information about the chemical composition of the surface as the absorption associated with this region is due to fundamental vibrations of a particular functional group. Table 6 lists mid-infrared absorption of important ions. Figure 3 is a laboratory spectrum of black

Vermont marble before and after exposure to about 160 $\mu g/M^3$ of SO_2 in air of relative humidity 100% at 60°C for 72 hours. The sulfate peak would correspond to less than 80 ng SO_4^{-2} per cm^2 of area.

Chemistry for Stone and Metal Samples

We discussed chemical spot test methods above as non-mechanical techniques which involve blotting the resource surface and observing a color change on an appropriate substrate. Implementation of the chemistry will involve some trial, especially in determining reagent life times in field conditions. Our implementation of the chemistry alluded to above has been using surface scrapings and a spot plate. The spot plate is a white ceramic plate with depressions which will contain about 0.75 ml. Analysis proceeds by scrapping a quantity of surface material from a defined area and placing it in the plate, then adding 1 N HCl to dissolve or leach those ions of interest from the sample.

Nitrate (NO_3^-) is determined using chromotropic acid reagent. The acid soluble constituents of a surface scraping are brought into solution with 1 N HCl on the spot plate. Two drops of chromotropic acid solution are added. Yellow color in 2-4 minutes indicates nitrate and nitrite. The intensity of the color is proportional to the concentration.

Sulfate (SO_4^{-2}) is determined by precipitation as barium sulfate ($BaSO_4$) which includes potassium permanganate ($KMnO_4$) in the lattice giving the precipitate a pink color. This is

known as the Wohler effect (9). It may be carried out in the spot plate but our implementation has been on filter paper. A surface scraping is taken into a plastic vial. A few drops of 1 N HCl are added to dissolve or leach sulfate from the sample. This solution is taken up with a 25 mm filter paper. 1 drop of $KMnO_4$ solution is placed on the paper. The paper is placed on the spot plate for 2-4 minutes. The paper is then rinsed with distilled water followed by oxalic acid. A pink color indicates sulfate. Figure 2 is a positive test for sulfate, the intensity of the color is proportional to the amount of sulfate present. A spot plate is visible in the background of figure 2. Color development methods for other ions are those described for spot tests (Table 4).

Implementation will require development of color standards, defining analysis procedures, reagent shelf life and determining procedures to be followed in a step wise manner depending upon whether stone or metal is being analyzed.

Hach Chemical Company markets kits for water and waste water analysis (10). Some of these kits contain color wheels which allow for comparison of sample color with a standard. They also market a portable laboratory which contains a colorimeter with turbidimetry accessory, pH/ISE meter, and conductivity probe, discussed below. These are listed in Table 5. We have indicated those which would be useful for stone or metal samples. Table 8 lists chemistry accessories.

Physical Test for Stone and Metal

We have selected methods for making observations of

changes in physical properties which are generally agreed to be important in the deterioration of metal and stone. The parameters measurable are surface roughness and gloss for stone/masonry and metal; and grain adhesion and water porosity for stone/masonry. Table 7 is a summary of physical test methods with associated parameters and cost estimates for kit components. Changes in physical properties are incurred as a result of chemical changes in the material fabric. Stone or masonry core samples taken mechanically may be analyzed at a laboratory for surface area, porosity and pore size using gas adsorption or mercury intrusion (11). These techniques are based on adsorption/desorption isotherms of an adsorbed gas, usually nitrogen (N_2), or on the penetration of a porous sample with liquid mercury. Implementation of either laboratory method will be useful in establishing calibration factors for the suggested field method of measuring water adsorption or stone/masonry porosity changes. We may find that an estimated pore volume is uniquely associated with water absorption times for a particular stone or masonry type.

The water absorption method referred to above is suggested by Commission 25-PEM (12). Porosity of stone/masonry to water is a very important parameter relating to deterioration. The degradation process occurs by dissolution of the material fabric, subsequent percolation and recrystallization tends to increase stone porosity allowing fresh surface to

be exposed. Implementation of this novel technique requires fabrication of a tube of reasonable diameter and volume. The tube is open on both ends and fixed to the surface with a suitable sealant such as rubber cement (this appears to be removable with no residue remaining). The tube may be fashioned for use with horizontal or vertical surfaces. The rate of absorption of water from the end of the tube into the surface is measured by filling the tube with a known volume of water and recording the time required to absorb this amount.

Grain adhesion may be used as an indicator of surface deterioration. In masonry materials, deterioration proceeds by dissolution of the material fabric due to various chemical processes. One result of this dissolution is a loss of adhesion of surface grains. ASTM reports a method (13) for paint adhesion requiring the use of a tape to pull material from a specific surface area. This method is adaptable to stone without modification. Replicating tape may also be used to remove granular surface material. Use of replicating tape would allow that the granular material could be archived or sent for analysis by SEM/EM. The parameter measured in the field would be the number of adherent particles per unit of surface area. Implementation would proceed by comparing the two methods as to precision.

Physical methods for stone and metals which are a measure of the depth and prominence of valleys and peaks

on the material surface are gloss and surface roughness.

Gloss is a specialized method for measuring the degree of specular reflectance from a surface. This important characteristic defines the subjective appearance of an object. Gloss is the surface attribute responsible for the shiny or lustrous appearance of an object. The degree of gloss is due to the directionally selective reflecting properties of a surface. Gloss meters are widely used in the paint industry (14) for measuring specular reflection intensity at 20, 60 and 85^{o} from the angle of incidence of a light source. Other angles are used for other materials. Implementation will require selecting the specular angles for the material of interest and standards for gloss references.

Surface roughness, although related to diffuse reflectance and gloss, may be measured directly. We suggest the following methods for assigning values to this parameter. The thickness of a piece of replicating tape may be measured with a micrometer by placing it between two glass slides or other suitable material. A surface replica may be taken (no adherent particles) and the thickness measured again. The difference in the two measurements would be indicative of the valley depth. Implementation would require selection of a suitable material for use as the outler layers and some trial as to the resolution. The tape may then be archieved or sent for detailed analysis of surface morphology by SEM.

A technique developed in our laboratory (15) for measuring the roughness of steel surfaces is directly applicable to other materials. The field microscope consists of a cylinder fitted with 200X magnifying optics which is placed against the surface. A light source is placed such that incident light strikes the surface at a known angle (20^{o}). The optics are equipped with a vernier scale and the viewing end may be fitted to an eye piece or adapted to a standard 35 mm camera mount. The height of surface feature may be calculated by measuring the length of the shadow and knowing the angle of incidence of the light. Photographs may be archived for future reference. Grain size may be measured and microscopic pitting may be observed in addition to lengths of shadows. Presently a white light source is used but adaptation to approximate monochromatic sources is readily feasible. This device is currently under development but prototypes have proven extremely useful in characterizing steel surfaces.

The Keane-Tator surface profile comparator (14) consists of a five section disc. Each section is of differing roughness and is assigned a number. The surface compared is viewed through the hole with a magnifying glass and assigned a number corresponding to the section of the disc most closely resembling the surface. A similar device could be constructed for stone types and metal patinas, implementation would require that standards be prepared.

Field Portable Instruments

Solid samples taken by scraping can be analyzed semi-quantitatively at the site using field portable instruments. We avoid balances for weighing because field portable instruments are delicate and require periodic maintenance. As we discussed above, an area may be scraped and that area measured to give a semi-quantitative value.

Chemical analysis would be performed by obtaining a set of samples and treating each with specified stock solutions for the ions of interest. The color development reagents for instrumental analysis are anticipated to be the same as discussed above. Solution mixing may be accomplished using disposable syringes. The sample solution is then introduced into the sample cell of a portable spectrophotometer. The Hach portable laboratory is referenced in Table 5, however other vendors supply similar instruments at comparable cost. The use of a spectrophotometer would allow for assignment of an absorbance value for the analyte solution which would be archived with the total sample area.

Tristimulus colorimeters are available with fiber optic probes which would play a dual role as a kit component. The surface color parameters (X, Y, Z) may be assigned directly. Also, the instrument may be used for associating X, Y, Z values with colors developed in the chemical spot test. Implementation would require that appropriate substrates be selected and factors be defined which associate these values

with a concentration of a particular ion. Commercially available instruments may be modified for field use.

Conductivity meters with temperature compensated probes are available for measuring the total quantity of dissolved salts in an aqueous sample. This quantity would be measured by scraping an area of the surface, adding a known quantity of water, then measuring the conductivity of the resulting solution. These meters are rugged and battery powered. Alternatively a moisture sensor such as is used in greenhouses for soil moisture measurments may be used. The latter is cheap and available but implementation would require some trial.

Field portable pH/ion specific electrode meters are available. Micro electrodes are available which require less than 1 ml of solution for determination of pH, Cl^-, NO_3^- + NO_2^-, $Ca^{+2} + Mg^{+2}$, and S^{-2}. Implementation would be similar to conductivity measurement. Conductivity, and pH may be measured from the same sample. The liquid sample would then be divided in a quantitative manner and prescribed reagents added to measure other ion concentrations. This technique is particularly attractive for Cl^- and S^{-2} as it is quite simple and virtually no other ions interfere.

Radiometers are used for making measurements of diffusely reflected radiation from stone or metal samples. Due to the effects of surface roughness and surface particle size, their use is generally limited to remote sensing for

qualitative identification of minerals. Commercial radiometers are usually classed as NIR (<2.5 μm) and mid-IR (> 2.5μm) due to transmission optics and detector type. Both are commercially available. NIR spectral reflection phenomena consists of combinations and overtones of longer wavelengths, the most intense absorption is due to water. We would not anticipate that NIR will provide useful information about the chemical composition of a deteriorating surface due to the inherently weak absorption of the species of interest relative to water.

Development of diffuse reflectance methods in the mid-IR region (>2.5μm) has potential for providing quantitative information concerning the relative surface concentrations of absorbing species. Implementation would proceed by comparing surface concentrations measured by diffuse reflectance to an established surface method e.g. SEM/XRA to define the limits of the method. A suitable radiometer incorporating an infrared illumination source with variable geometry and optics for near surface (a few cm) could be designed. Overall design criteria would be similar to the radiometer designed under our concurrent DOE contract (16).

III. FIELD KIT OPTIONS

We have selected field kit options for high, low and medium cost kits. Cost of kit components is estimated from appropriate tables in Section II. Kits containing field portable instruments will generally result in less ambiguous observations. The cost per kit would be higher than a visual comparison, but the results would tend to be more objective.

KIT OPTION A

Replication tools	$110
Water absorption apparatus	10
Scraping tools	30
Spot Test	200
Camera	50
Packaging and guidebook for stone or metal resources	150
	$550

We estimate this cost per kit based on 10 kits produced. Capabilities are for:

1) chemical spot test
2) porosity to water
3) grain adhesion
4) surface roughness
5) sampling for archives/laboratory analysis

We estimate training time for use at 8-16 hours.

KIT OPTION B

Replication tools	$ 80
Water absorption apparatus	10
Scraping tools	30
Chemistry accessories (color charts)	500
Field Microscope	325
Camera	50
Conductivity meter	500
pH meter	275
ISE meter	1100
Packaging, guidebook for stone and metal resources	250
	$3120

We estimate $3120 for the medium cost kit based on 10 kits produced. Capabilities are for:

1) semi-quantitative chemistry
2) porosity to water
3) surface roughness
4) total ion concentration
5) grain adhesion
6) sampling for archives/laboratory analysis

We estimate training time for use of these components at 8-16 hours.

KIT OPTION C

Replication tools	$ 80
Water absorption apparatus	10
Scraping tools	30
Portable spectrophotometer reagents	2000
pH meter	$ 275
ISE meter	1100
Glossmeter	1000
Conductivity meter	500
Colorimeter (X,Y,Z)	2000
Camera	50
Packaging and guidebook for stone and metal samples	700
	$7745

We estimated this cost per kit based on 10 kits produced.

Capabilities are for:

1) Sampling for quantitative chemistry
2) Non-destructive quantitative observations
3) Sampling for archive/laboratory analysis
4) Surface roughness
5) Total ion concentration
6) Grain adhesion
7) Water porosity

We estimate 16-24 hours of instruction would be required for use of this kit by Park Service personnel.

IV. SUMMARY AND CONCLUSIONS

The field kit is intended for National Park Service resource managers to allow them to monitor materials deterioration in their areas. While particular emphasis is placed on acid precipitation effects, the kit is generally applicable to monitoring surface deterioration by any mechanism. The kit will be low in cost and in technical complexity, designed for use by non-technical personnel.

The measurement of the surface condition of stone and metal involves both chemical and physical characterization. Chemical spot tests are used for on-site semiquantitative measurement of pH, chloride, and sulfur and nitrogen compounds. For cases requiring more detailed analysis, tools and containers are included for removing a sample and sending it for laboratory analysis.

Physical characterization utilizes field techniques for measurement of surface roughness, for preparation of a surface replica, and for magnified optical examination. More precise characterization, if needed, can be obtained from the replica using optical or electron microscopy at a central laboratory

Carefully defined procedures and effective training aids are important components of any effective kit. Further refinement of this design will require actual construction of a prototype kit and a series of field trials.

Park Service personnel with good mechanical skills and physical science exposure at the level of high school chemistry and physics should be adept at making measurements using kit components with less than 24 hours instruction.

The development cost presented in Tables 1, 7, and 9 are best estimates based on August 1983 costs. The kit component costs are derived from production of 10 field kits containing this component. Generally high kit component costs are associated with lower development cost as the higher cost is for a commercially available instrument.

VI. TABLES AND FIGURES

Technique	Level of Damage	Chemical Property	Equipment Required	Analysis at Site	Sample Type	Observation Method	Estimated Cost for Development	Cost as a Component
)ptical	none	color	color charts	yes	S,M	visual comparison to standards	$25,000	$ 200
)ptical	none	color	colori-	yes	S,M	X,Y,Z color coordinates	10,000	2000
				yes	S,M	intensity of reflected radiation	50,000	4000
				yes	S,M	comparison to standards	20,000	200
				no	S,M	X-ray analyzer	none[a]	80
			arts te	yes	S,M	visual comparison to standards	20,000	500
Scraping	small	quantitative chemical composition	portable spectrophotometer reagents	yes, semi-quantitative	S,M	instrumental	8,000	3000
Coring	medium	quantitative chemical composition	Ion chromatography Laboratory spectrometer	no	S,M	instrumental	none[b]	150

a) analysis $100/sample

b) analysis $25/sample

Table 1. Surface sampling and analysis for chemical properties. S = stone, M = metal.

Table 2. Mechanical Sampling Tools

REPLICATION	ITEM COST
Replicating tape	$ 7.00
Replica solution	5.00
Brush	3.00
Droppers (disposable)	5.00
Acetone (500 ml)	9.00
Tweezers	7.50
Scissors	6.00
Single edge razor blades	1.00
Storage boxes	10.00
Dust-off (canned air)	15.00
Magnifying glass	7.00
Pick	2.00
SCRAPING	
Chemi-scraper	3.25
Scoop spatula/handle	3.00
Plastic bag (12)	3.00
Plastic vial (12)	2.40
Filter paper	2.50
Template	12.00
CORING	
Bits (set)	55.00
Drill (battery powered)	60.00
CAMERA	50.00

Table 3. Materials for Non-mechanical Sampling

	Item Cost
pH paper (3.5 to 5.5)	$ 5.40
Lead sulfide paper	1.40
Filter paper (25 μm)	2.25
[a,b] Reagents for Sulfate	18.00
[a,b] Reagents for Chloride	24.00
[a,b] Reagents for Nitrate	30.00
Storage dropper bottles	12.40
[b] Color charts for spot test	--
[b] Color comparison charts for stone	--
[b] Color comparison charts for metal (bronze)	--

a) Estimated materials cost

b) Development cost dependent upon implementation scheme (See Table 1).

Ion Confirmed	Chemical Spot Test Method	Estimated detection limit ($ng\text{-}cm^{-2}$) *	Color of Positive Test
NO_3^-	Chromotropic acid	0.5	yellow
SO_4^{-2}	Wohler effect	0.1	pink
NH_4^+	Indophenol blue	2.0	blue
Cl^-	Silver nitrate paper	10	gray/black
S^{-2}	Lead acetate paper	10	black
H^+	pH paper (3.5-5.5) pH paper (1-14)	(.5 pH unit) (1 pH unit)	interpret color from chart

* minimum concentration required to give a positive visual test.

Table 4. Chemical Spot Test

Table 5. Hach Kits (catalog numbers)

	Cost
Portable laboratory (DR-EL/5) colorimeter, conductivity, pH meters and accessories, requires ISE.	$1675.00
[a]Low range nitrate kit (NI-14)	41.00
[a,b]Nitrate/Nitrite kit (NI-12)	64.50
[a,b]Ammonia test kit (NI-8)	33.50
[a]Sulfide test kit (HS-6)	82.50
[a]Chloride test kit (CD-DT)	115.00
[a]pH test kit (17D)	45.50
[b]Sulfate test kit (SF-1)	38.50

[a]These kits include a color wheel for comparing the color developed with a standard. This quantification method is typically reproducible to about 5%.

[b]Not for use with stone or metal samples.

Table 6. Infrared Absorption of Selected Ions

Anion	Absorption Peak Region (micrometers, μm)
CO_3^{-2}, Carbonate	6.8 - 7.2; 11.3 - 11.7
SO_4^{-2}, Sulfate	8.5 - 10.0; 14.7 - 16.5
NO_3^-, Nitrate	6.0 - 8.0; 11.5 - 13.0
NO_2^-, Nitrite	8.0 - 8.2; 11.9 - 12.5
NH_4^+, Ammonium	3.0 - 3.3; 6.8 - 7.5
Silicates	9.0 - 11.5

Technique	Level of Damage	Physical Property	Equipment Required	Analysis at Site	Sample Type	Observation Method	Estimated Cost for Development	Estimated Cost as a kit Component
Replication	almost none	surface morphology	SEM replication kit	No	S,M	electron microscopy	none	$80[b]
Replication	almost none	grain adhesion	magnifying lens replication kit rule	Yes	S(M?)	number of particles adherent per cm^2	$2000	$100
Replication	almost none	surface roughness	micrometer replication kit	Yes	S,M	depth of surface valleys	$2000	$110
Water absorption	almost none	water porosity	suitable apparatus (text)	Yes	S	time for ml/cm^2 absorbtion	$3000	$ 10
Adhesion test	almost none	grain adhesion	ASTM adhesive tape	Yes	S(M?)	number particles adherent per cm^2	$1000	$ 10
Gloss	none	relative surface roughness	gloss meter	Yes	S,M	intensity of specular reflection	$5000[a]	$1000
Comparator	none	relative surface roughness	comparator standard magnifying lens	Yes	S,M	compare surface to a standard surface	$25000	$250
Shadow length	none	surface roughness	field microscope	Yes	S,M	height of surface peaks	$3000[a]	$325

a) include purchase/modification of one instrument, b) $100/sample for analysis.

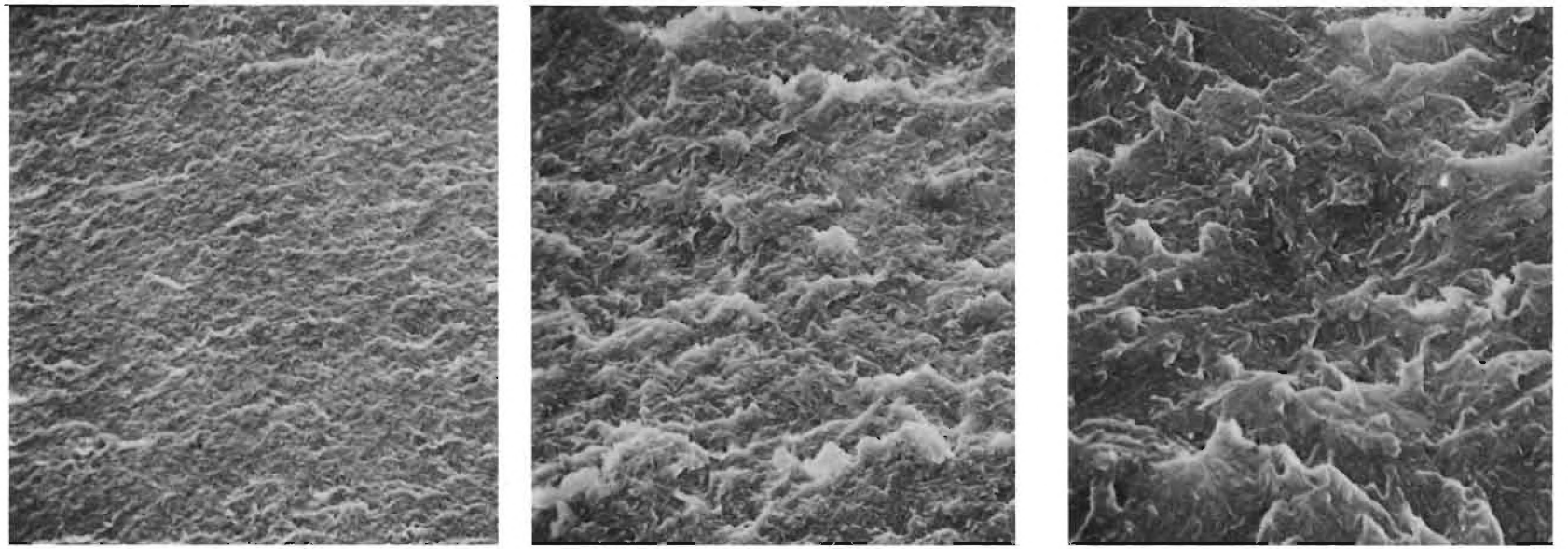
Table 7. Surface sampling and analysis for physical properties. S = stone, M = metal. (M?) may be adaptable to metal.

Table 8. Accessories for field chemistry. (See Tables 1-3 also).

	ITEM COST
dial thermometer	$ 6.00
magnifying glass	7.00
ruler/template	15.00
weighing paper	2.50
micro-spatula	2.50
disposable pipets (1 cc, 10 cc)	.20 each
plastic vials (50 ml)	.75 each
syringes (1 cc, 10 cc)	.50 each
Tygon tubing	1.00
spot plate	12.00
filter paper	2.20

Type of Instrument	Chemical/Physical Property Measured	Available Portable	Observation Method	Sample Type	Anticipated Sampling Technique	Estimated Cost for development	Estimated Cost as a kit Component
Spectrophotometer	semiquantitative chemistry	Yes	digital absorption of solution	S,M	Scraping	$8,000	$2,000
pH meter/probe	pH	Yes	digital pH indication	S,M	Scraping	$ 500	$ 275
Ion Selective Electrode and meter	chloride, sulfide	Yes	digital concentration indication	S,M	Scraping	$2,500	$ 1100
Ion Selective Electrode and meter	nitrate, and nitrite ammonium calcium, magnesium	Yes	digital concentration indication	S,M	Scraping	$10,000	$ 1100
Conductivity meter	total water soluble ion concentration	Yes	digital ion concentration indication	S,M	Scraping	$2,500	$ 500
Tristimulus Colorimeter	color	Not at present	X, Y, Z chromaticity	S,M	none	$12,000	$ 2000
Glossmeter	surface roughness	Yes	Angular distribution of reflected visible light	S,M	none	$5,000	$ 1000
Field Microscope	surface roughness	Yes	shadow length	S,M	none	$3,000	$ 325
Radiometer, 2.5 - 20 μM	Chemical composition	Yes	intensity of reflected radiation	S,M	none	$50,000	$ 4000

Table 9. Instruments adaptable for field measurements. Development cost includes purchase/modification of one instrument.



120X 600X 2400X

Magnification:

Figure 1. SEM of a metal surface replica.

Figure 2. A positive test for sulfate, a spot plate is in the background.

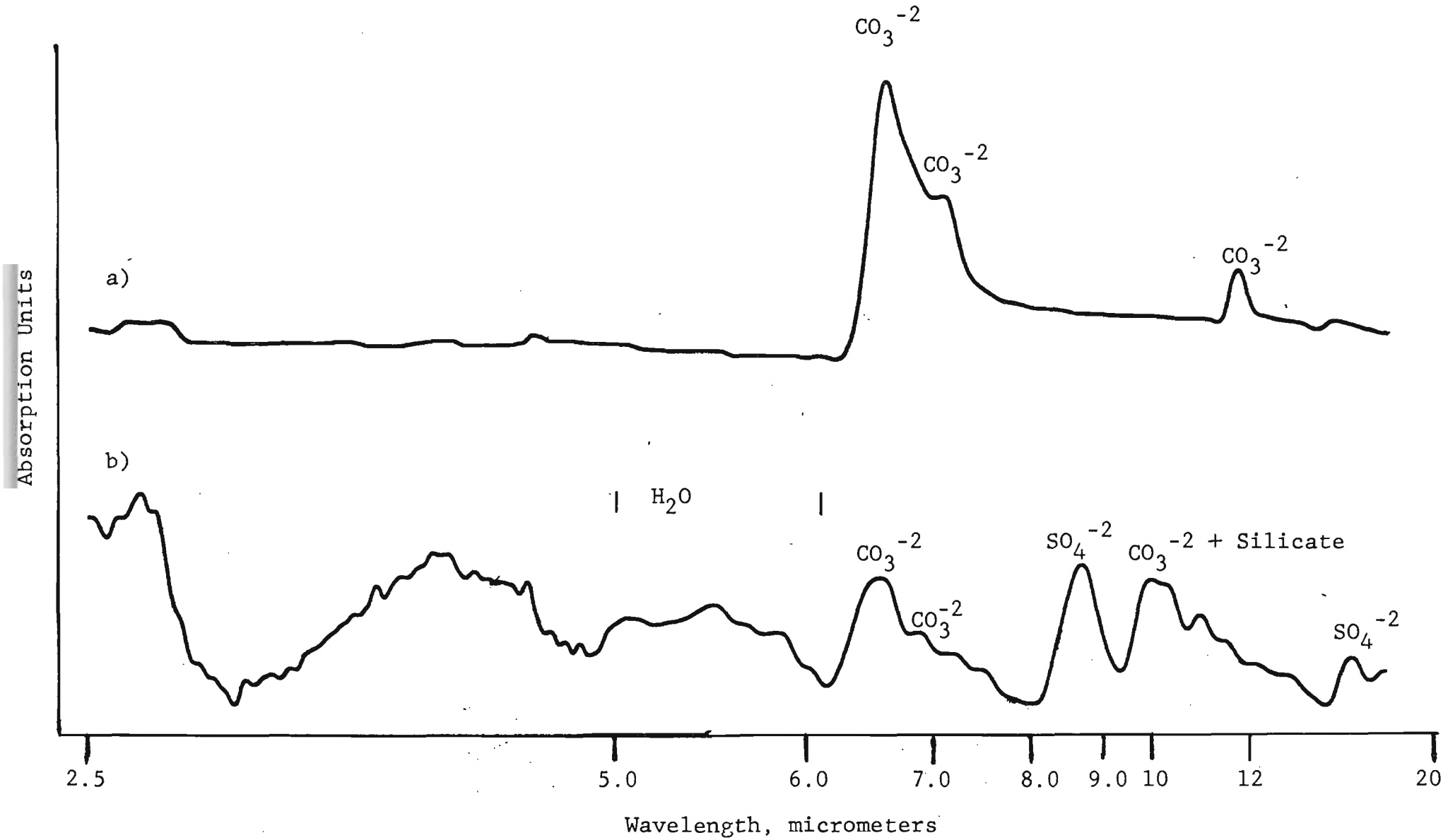


Figure 3. Infrared diffuse reflectance of a) Polished Black Vermont Marble, and b) the same sample upon exposure to SO_2/H_2O/Air microclimate at 60°C for 72 hours. Reference was a gold diffuse reflector standard.

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